Study on the Dynamic Viscosity of Diethylene Glycol Dimethylether up to 100 MPa

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Abstract

The work reports new, preliminary measurements of the viscosity of liquid diethylene glycol dimethylether (DEGDME) up to 100 MPa at eight temperatures ranging from 293.15 to 353.15 K. The measurements at atmospheric pressure have been performed with an Ubbelohde-type glass capillary tube viscometer with an uncertainty of ±1%. At pressures up to 100 MPa the viscosity was determined with a falling body viscometer with an uncertainty of ±2%. The present measurements were used to develop empirical correlations for these compounds and also to study the chain length dependence of the viscosity. The prediction capability of models with physical background (hard-sphere scheme and free-volume model) has been tested from other previous polyalkylene glycol dimethylether viscosity and density data.

Keywords: falling-body viscometer, high pressure; polyethylene glycol dimethylethers; viscosity.

1. Introduction

In the last years measurements of the viscosity of polyalkylene glycol dimethylethers, $CH_3O-((CH_2)_2O)_n-CH_3$, under pressure have become important because of the use of these data in studying the reliability of these fluids as lubricants in refrigeration compressors and as absorbents for absorption systems. However, the database for thermophysical properties of these compounds, at present, is scarce and at very limited temperature and pressure conditions. Most measurements have been made at atmospheric pressure and at temperatures in the range from 293.15 to 323.15 K. Thus, while there are abundant data, for these compounds, describing the temperature dependence of the viscosity at 0.1 MPa [1-4], studies versus pressure are less frequent. Only in our previous works [5, 6] the dynamic viscosity at high pressure of triethylene glycol dimethylether (TriEGDME) and tetraethylene glycol dimethylether (TEGDME) have been measured.

To complete our experimental [5, 7-9] and theoretical studies [6] of some physical properties of polyethylene glycol dimethyl ethers, in this paper we report new viscosity data of DEGDME at temperatures from 293.15 to 353.15 K and at pressures up to 100 MPa.

2. Experimental Section
2.1. Measurement Techniques

The principle of measurement, the apparatus (an Ubbelohde-type glass capillary-tube viscometer with a Schott-Geräte automatic measuring unit Model AVS 350 and a falling body viscometer for high pressures) and the experimental procedure for the viscosity determination are described in details in our previous work [5] concerning the measurements of these properties for tetraethylene glycol dimethylether (TEGDME) and triethylene glycol dimethylether (TriEGDME). The experimental uncertainties are 1% for dynamic viscosity at atmospheric pressure and 2% for dynamic viscosity at high pressures. In order to measure the
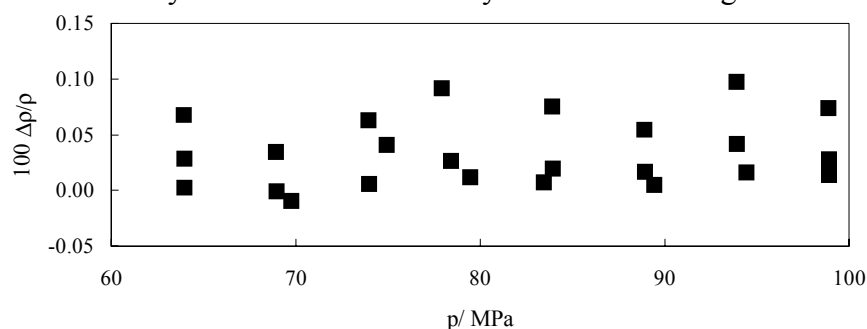
viscosity up to 100 MPa, the density values is needed, so, the experimental density values reported from 293.15 to 353.15 K and at pressures up to 60 MPa, have been used [10]. The Hogenboom modification of the Tait equation [11] was used, as in the previous paper [5], for density extrapolation at pressures higher than 60 MPa and up to 100 MPa.

2.2. Materials

Diethylene glycol dimethyl ether, DEGDME, (molar mass 134.18 $g \cdot mol^{-1}$) was obtained from Aldrich with a purity of 99.5%. This product was subjected to no further purification.

3. Results

The extrapolated density values up to 100 MPa obtained by using the Hogenboom modification [11], have been compared with the literature values reported by Sharipov and Bairamova [12]. In figure 1, the deviations between both data sets can be observed. For pressure between 60 and 100 MPa, the extrapolated values agree with the literature ones with an average absolute deviation of 0.05% for DEGDME, and with maximum absolute deviations of 0.15%. In this sense it is interesting to point out that an error of $\pm 1 \cdot 10^{-2}$ $g \cdot cm^{-3}$ generates a relative error of 1/800 for viscosity. We have seen that the density extrapolation from 60 MPa to 100 MPa yielded an error markedly less than $\pm 1 \cdot 10^{-2}$ $g \cdot cm^{-3}$.


Figure 1. Deviations between the extrapolated densities of DEGDME up to 100 MPa and the literature values reported by Sharipov and Bairamova [12].

The experimental dynamic viscosity values at different pressures and temperatures are listed in Table I. To our knowledge there are no literature viscosities for this fluid at pressures different from the atmospheric value. Ku and Tu [1] have published experimental measurements at 0.1 MPa and at different temperatures between 288.15 and 343.15 K. The average deviation of our measurements from their values is 0.4% for DEGDME. Our experimental values agree with those published by Conesa et al. [3] with an average deviation of 1.2%. These deviations are consistent with the uncertainty of the experimental apparatus at 0.1 MPa.

Figures 2-4 illustrate the variations of the dynamic viscosity versus temperature and pressure of DEGDME (n=2) along with the values previously obtained [5] on Triethylene Glycol Dimethylether (TriEGDME, n=3) and Tetraethylene Glycol Dimethylether (TEGDME, n=4). It can be observed that the viscosity decreases with the temperature and increases with the pressure for each of the three compounds. In addition, the viscosity increases as the chain length of the polyalkylene glycol dimethylether increases.

|	T/K						
p/MPa	293.15	303.15	313.15	323.15	333.15	343.15	353.15
0.1	1.1039	0.9309	0.8134	0.6953	0.6329	0.5612	0.4860
20	1.2669	1.0725	0.9290	0.8118	0.7439	0.6500	0.5769
40	1.4576	1.2243	1.0595	0.9402	0.8532	0.7485	0.6668
60	1.6671	1.3899	1.2020	1.0720	0.9654	0.8531	0.7566
80	1.8890	1.5671	1.3529	1.2019	1.0793	0.9607	0.8440
100	2.1195	1.7539	1.5100	1.3265	1.1935	1.0692	0.9276

Table I. Experimental Dynamic Viscosity of DEGDME versus temperature T and pressure p.
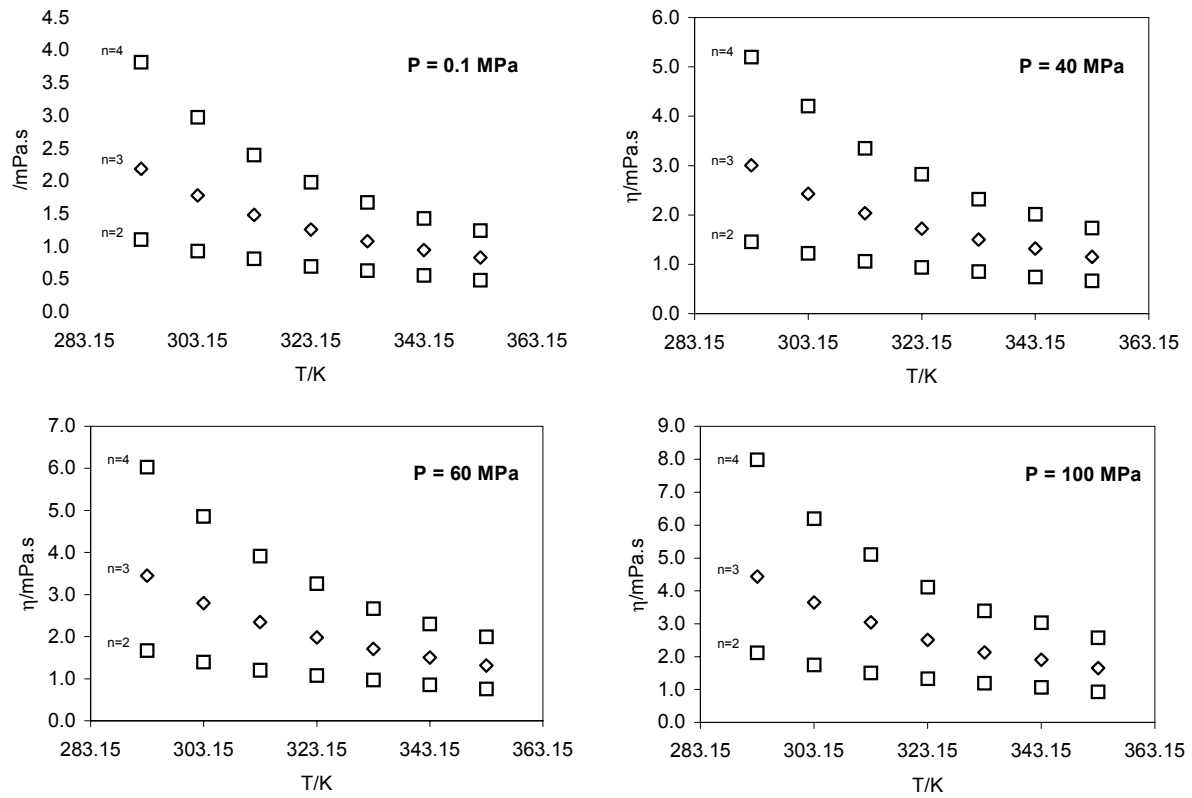
Figure 2. Variation of dynamic viscosity of several polyethers, $CH_3O-((CH_2)_2O)_n-CH_3$, versus temperature for various pressures. This work n=2, ref [5] n=3, 4.
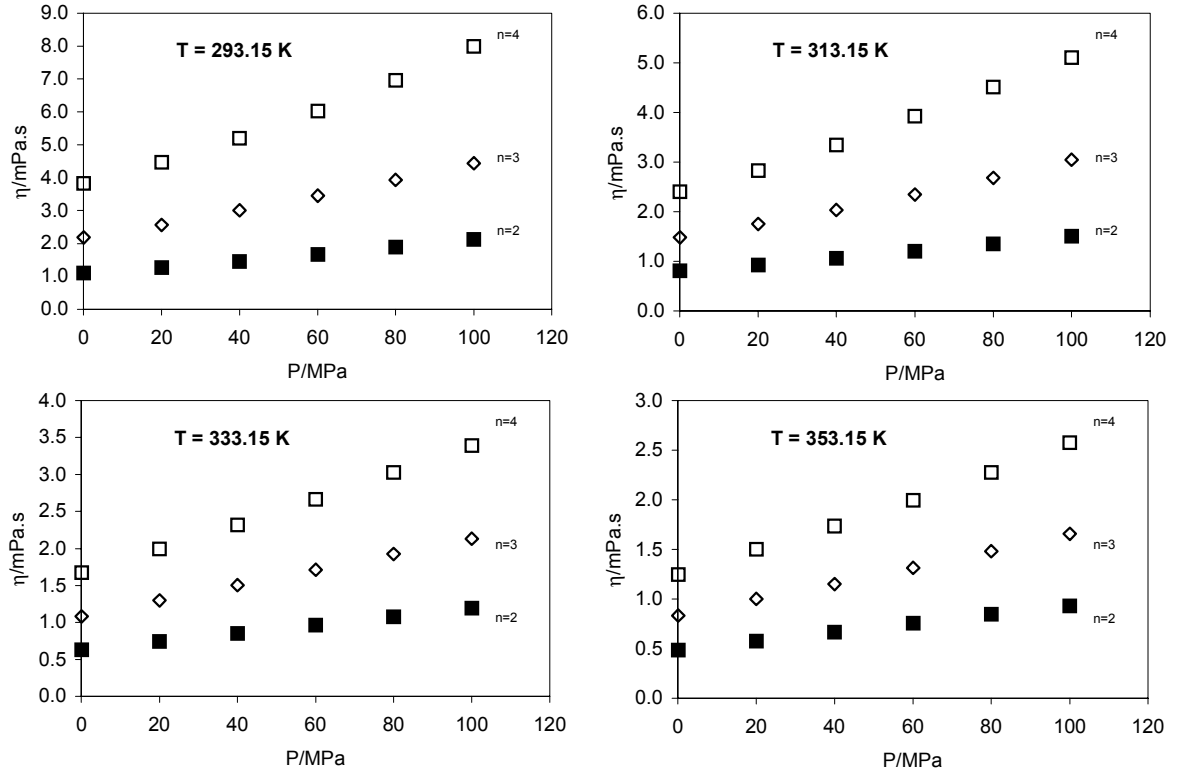
Figure 3. Variation of dynamic viscosity of several polyethers, $CH_3O\text{-}((CH_2)_2O)_n\text{-}CH_3$, versus pressure for various temperatures. This work n=2, ref [5] n=3, 4.
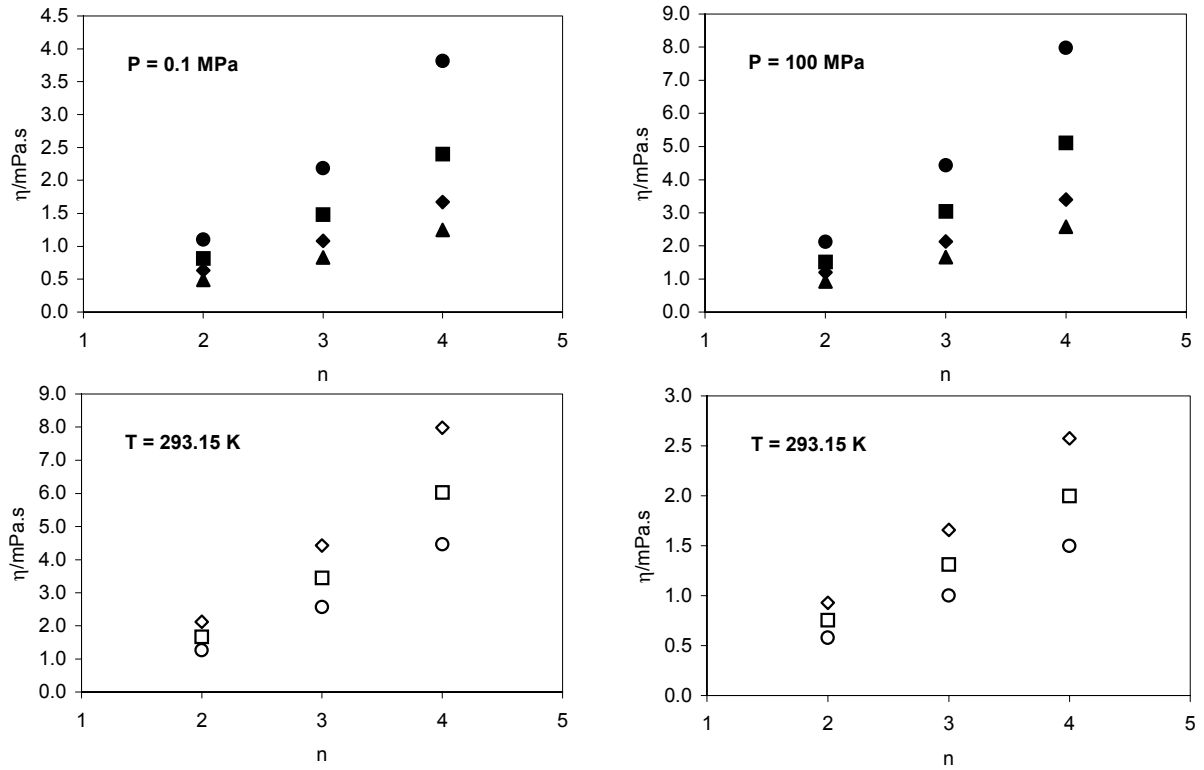
Figure 4. Variation of dynamic viscosity of several polyethers, $CH_3O\text{-}((CH_2)_2O)_n\text{-}CH_3$, versus n at 0.1 and 100 MPa(●:293.15, ■:313.15, ◆:333.15 and ▲:353.15 K) and at 293.15 and 353.15 K (○:20, □:60 and ◇:100 MPa). This work n=2, ref [5] n=3, 4.

4. Viscosity representations
4.1. Andrade representation
The experimental data of viscosity on an isotherm, $\eta(p)$ can be fitted for each isotherm to the following Tait-like equation:

$$\eta(p) = A \exp\left[B \ln\left(\frac{C+p}{C+0.1\,\text{MPa}} \right) \right] \qquad (1)$$

and on an isobar $\eta(T)$ can be fitted for isobar to the following Andrade's equation [13]:

$$\eta(T) = A \exp\left(\frac{B}{T-C} \right) \qquad (2)$$

Both previous equations can be combined in order to fit the viscosity as a function of temperature and pressure. We then propose the following equation:

$$\eta(p,T) = \eta_0(T) \exp\left[D \ln\left(\frac{E(T)+p}{E(T)+0.1\,\text{MPa}} \right) \right] \qquad (3)$$

where $\eta_0(T)$ is the temperature dependence of the viscosity at the reference pressure and is given by Eq. (2). Therefore, from Eqs. (2) and (3) one obtains the following equation,

$$\eta(p,T) = A \exp\left[\frac{B}{T-C} \right] \exp\left[D \ln\left(\frac{p+E(T)}{0.1\,\text{MPa}+E(T)} \right) \right] \qquad (4)$$

where D was assumed to be temperature independent and $E(T)$ is a second-order polynomial. Using this equation (involving seven parameters) we have obtained an average absolute deviation of 1.16% for DEGDME. The maximum deviation is 4.62% at 353.15 K and 100 MPa.

4.2. The Hard Sphere Scheme
4.2.1. Presentation of the model
Recently [14, 15] a scheme has been developed for the simultaneous correlation of self-diffusion, viscosity and thermal conductivity of dense fluids. The transport coefficients of real dense fluids expressed in terms of $V_r = V_0/V$ with V_0 the close-packed volume and V the molar volume, are assumed to be directly proportional to values given by the exact hard-sphere theory. The proportionality factor, described as a roughness factor R_η accounts for molecular roughness and departure from molecular sphericity. Universal curves for the viscosity were developed and are expressed as:

$$\text{Ln}\left(\frac{\eta^*_{\text{exp}}}{R_\eta} \right) = \sum_{i=0}^{7} a_{\eta i}(1/V_r)^i \qquad (5)$$

with $\qquad \eta^*_{\text{exp}} = 6.035 10^8 \left(\frac{1}{MRT} \right)^{1/2} \eta_{\text{exp}} V^{2/3}$

It seems [16] that the coefficients $a_{\eta i}$ are universal, independent of the chemical nature of the compound. For alkanes [15] and aromatics [17] the authors give correlation formulas relative to V_0 and R_η. For a given compound parameters V_0 are temperature dependent whereas R_η is a constant

4.2.2. Results
In our case, parameters V_0 and R_η are not available in the literature, for this reason, we have applied the hard-sphere model keeping constant the universal coefficients $a_{\eta i}$ of Assael *et al.* [15,17] and calculating the coefficients R_η and V_0 for each temperature for DEGDME and

also for TriEGDME and TEGDME. We have fitted the parameters minimizing the absolute average deviation over a set of 42 experimental viscosity data for each compound.

The obtained parameters values and the results for this model are presented in Table II. It can be observed that the absolute average deviations are below than the experimental uncertainty.

Parameters				
Universal Parameters	Liquid	DEGDME	TriEGDME	TEGDME
$a_{\eta k}$	T/ K	V_o $(10^{-4}$ m^3.mol^{-1})		
1.0945	293.15	0.97247	1.29814	1.62280
-9.2632	303.15	0.96313	1.28817	1.61181
71.0385	313.15	0.95712	1.27938	1.59866
-301.9012	323.15	0.95122	1.26923	1.58689
797.6900	333.15	0.94677	1.26092	1.57370
-1221.9770	343.15	0.93965	1.25452	1.56595
987.5574	353.15	0.92998	1.24525	1.55458
-319.4636		Rη		
		1.6006	1.9221	2.3039
	Results			
Deviations (%)	Overall	DEGDME	TriEGDME	TEGDME
AAD	0.93%	0.87%	0.73%	1.17%
Bias	-0.14%	4.52%	3.83%	4.43%
DM	4.52%	-0.15%	-0.17%	-0.09%
N	126	42	42	42

Table II. Results obtained on the three compounds with the hard sphere scheme

A further step to the modeling of these three alkylene glycol dimethylethers was to represent the variation of the dynamic viscosity as a function of the number of CH_2-CH_2-O groups, n, which is equal to 2 for DEGDME, 3 for TriEGDME and 4 for TEGDME.

The parameters V_0 and R_η have been re-estimated, expressing them with a simple linear function, on the overall data set (126 points). The correlations used are the following:

$$V_0 = a_V \, n + b_V$$
$$R_\eta = a_R \, n + b_R$$

The results are presented in Table III along with the new parameters, which have been reduced from 24 to 16. A good representation is obtained as the absolute average deviations are around 1%, which is still below the experimental uncertainty and with maximum deviations lower than 6%.

Rη		V_0		
a_R	b_R	T/ K	a_V $(10^{-4}$ m^3.mol^{-1})	b_V $(10^{-4}$ m^3.mol^{-1})
0.488302764	0.498837627	293.15	3.18173	3.42229
		303.15	3.16316	3.37120
		313.15	3.12810	3.38533
		323.15	3.09268	3.39615
		333.15	3.03612	3.48224
		343.15	3.03155	3.42114
		353.15	3.01661	3.36753
Deviations (%)	Overall	DEGDME, n=2	TriEGDME, n=3	TEGDME, n=4
AAD	1.02%	0.97%	0.80%	1.29%
Bias	5.64%	3.51%	4.13%	5.64%
DM	-0.14%	0.12%	-0.36%	-0.18%
N	126	42	42	42

Table III. Results obtained on the three compounds with the hard sphere scheme and the correlated parameters.

4.3. The Free-volume Viscosity Model

4.3.1. Presentation of the model

Recently [18] an approach in order to model the viscosity of Newtonian fluids (in the condensed phase; density $\rho > 200$ kg.m^{-3}) with small molecules (not polymers for instance) has been proposed. This approach connects viscosity η to molecular structure via a representation of the free volume fraction. The viscosity, in this theory, appears as being the product of the fluid modulus $\rho RT/M$ by the mean relaxation time of the molecule defined by $N_a L^2 \zeta/(RT)$ and one can write viscosity in the form $\eta = \dfrac{\rho N_a \zeta L^2}{M}$ where N_a is the Avogadro number, ζ the friction coefficient of a molecule, and L an average characteristic molecular quadratic length. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process (diffusion of the momentum for viscosity). Moreover the free volume fraction is at the temperature T defined by $f_v = \left(\dfrac{2RT}{E}\right)^{3/2}$ assuming that the molecule is in a state such that the molecular potential energy of interaction with its neighbors is E/N_a. It has been assumed [18] that $E = E_0 + PM/\rho$ (P: pressure) where the term $PM/\rho = PV$ is connected to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and where E_0 is connected to the barrier energy which the molecule must cross to diffuse. R is the gas constant. Using the empirical relation of Doolitle $\eta = A\exp(B/f_v)$ where $f_v = v_f/v_0$ is the free volume fraction (v: specific molecular volume; v_0: molecular volume of reference or hard volume), and B is the characteristic of the free volume overlap, the combination of both equations leads to write ζ in the form $\zeta = \zeta_0 \exp(B/f_v)$ and thus:

$$\eta = \frac{\rho N_a L^2 \zeta_0 \exp(B/f_v)}{M}$$

But it has been demonstrated [18] that:

$$\zeta_0 = \frac{E}{N_a b_f}\left(\frac{M}{RT}\right)^{\frac{3}{2}}$$

where b_f is the dissipation length of the energy E. Finally:

$$\eta = \frac{\rho \ell \left(E_0 + \dfrac{PM}{\rho}\right)}{\sqrt{3RTM}} \exp\left(B\left(\frac{E_0 + \dfrac{PM}{\rho}}{2RT}\right)^{\frac{3}{2}}\right) \tag{6}$$

where $\ell = L^2/b_f$ is homogeneous with a length. This equation involves 3 physical parameters ℓ, E_0 and B, which are characteristic of the molecule. This model has been tested [28] using a database of 41 compounds of very different chemical families: alkanes (linear and ramified, light and heavy), alkylbenzenes, cycloalkanes, alcohols, fluoroalkanes (refrigerant), carbon dioxide and water. For the pressure range P < 110 MPa and density range $\rho > 200$ kg·m^{-3} (dense fluids) there are 3012 points in the database [18] and AAD = 2.8%.

4.3.2. Results

The parameters values and the results are displayed in Table IV. It must be noticed that the absolute average deviations for each of the compounds are lower than the experimental uncertainty with maximum absolute deviations lower or equal to 5.33% (obtained for the TEGDME). The overall results are then very good, with an absolute average deviation of 1.67%, if we consider that the calculations involve only 9 parameters.

Like for the hard sphere scheme, a reduction of the number of the parameters has been tested. Each main parameter ℓ, E_0 and B have been correlated against the chain length n, with linear equations of the type $x = a\,n + b$ ($x = \ell$, E_0 or B) so that only 6 parameters are used. The latter results and parameters are shown in Table V. The results are a little bit less good but the absolute average deviations are still of the order of the experimental uncertainty.

	Overall	DEGDME	TriEGDME	TEGDME
ℓ (Å)		0.27475	0.26092	0.21154
E_0 (kJ.mol^{-1})		105.5948	141.0109	182.7348
B		0.025081	0.019658	0.015806
AAD	1.67%	1.78%	1.39%	1.84%
Bias	-0.19%	0.30%	-0.33%	-0.55%
DM	5.33%	3.90%	4.64%	5.33%
N	126	42	42	42

Table IV. Results obtained on the three compounds with the free-volume viscosity model.

	a		b	
ℓ (Å)	-0.026516		0.336381	
E_0 (kJ.mol^{-1})	28.778		55.701	
B	-0.0022897		0.0264055	
	Overall	DEGDME	TriEGDME	TEGDME
AAD	1.93	2.20	1.41	2.18
Bias	-0.12	0.18	-0.60	0.07
DM	7.82	7.82	4.93	7.48
N	126	42	42	42

Table V. Results obtained on the three compounds with the free-volume viscosity model and the correlated parameters.

5. Conclusion

The dynamic viscosity of diethylene glycol dimethylether has been measured up to 100 MPa in the temperature range 293.15 to 353.15 K. The experimental uncertainty for the viscosity measurements is less than 2%, except at 0.1 MPa where the uncertainty is 1%. It follows from the discussion that some simple viscosity approaches with a strong physical and theoretical background (the hard-sphere scheme, the free-volume model) are able to model the viscosity of this compound as well as triethylene glycol dimethylether and tetraethylene glycol dimethylether within the experimental uncertainty. The correlation of the parameters against the chain length has been successfully considered. The experimental data obtained (126 points for the dynamic viscosity of the three compounds) could be included in databases and used to carry out further tests of other models more sophisticated, as for instance models based on molecular dynamic simulation.

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